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# Cogeled copper–silica aerogel as a catalyst in hydrogen production from methanol steam reforming

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## ABSTRACT

In this work, the copper–silica aerogel catalyst was prepared by cogelation of copper and silica precursors in a sol–gel process followed by chemical surface modification and ambient pressure drying. The results of characterizations by XRD, BET, FE-SEM, TEM, FTIR and TPR showed the prepared catalysts had high surface area and pore size distribution in the range of 1–10 nm. Also, uniform nanostructural morphology with particle size of 5–20 nm was observed. The copper loading and calcination temperature influenced the morphology and texture of the catalyst and the nature of copper species. So, copper existed within the silica matrix as highly dispersed isolated copper ions or CuO crystallite clusters which have good interaction with the matrix. Catalytic performance for hydrogen production from methanol reforming was evaluated at 300 °C in the methanol feed rate of 12–65 mmol g<sup>−1</sup> h<sup>−1</sup>. The catalyst activity was increased by increasing the copper loading and calcination temperature. In comparison with CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> commercial catalyst which showed 6–11% CO selectivity, no CO formation was detected using the prepared Cu/SiO<sub>2</sub> aerogel catalysts.

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## Introduction

Hydrogen fuel cells are a promising alternative to the internal combustion engines in the transportation application. Due to the safety and mechanical problems of the distribution and storage of hydrogen, the on-board hydrogen production from liquid hydrocarbons can be a practical option for the development of the fuel cell powered systems. Steam reforming of methanol has received particular attention to supply the hydrogen feed of the fuel cell [1–4].

In addition to the main products, hydrogen and carbon dioxide, a small amount of CO as undesired by-product can also be produced in MSR process. The presence of CO in the fuel cell feed causes poisoning of the platinum anodes of the fuel cell. Thus, the reformer gas requires further purification processes such as water–gas shift reaction followed by preferential CO oxidation. But, in these processes some of the produced hydrogen will be consumed and an excessive amount of oxygen is required. Also, the number of unit, complexity and cost of process will be increased. Therefore, development of new and more efficient catalysts with high selectivity and high hydrogen production rate is of interest to

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minimize the CO production, simplify the process and compact the fuel processing unit [5–8]. Various researchers have attempted to develop an efficient catalyst to this reaction. Copper containing catalyst show the highest activity and selectivity for MSR [5,9]. Silica-supported copper catalyst was used for MSR and shows good activity and significantly low CO selectivity [10,11]. Taking this into consideration, and due to the remarkable properties of the aerogels as catalytic applications including large surface area, good thermal stability, high open porosity and no mass transfer limitation of reactants [12–14], copper–silica aerogel catalyst was prepared for methanol steam reforming process.

Many investigations have been done on catalytic application of silica aerogels in which silica aerogel composites are generally derived through sol–gel process followed by supercritical drying of wet gels using silicon alkoxides as silica source [12–26]. However, alkoxides precursors are more costly and harmful. Also, supercritical drying is quite energy intensive, requires high temperature and pressures, and involves the heating and evacuation of highly flammable solvents, which is dangerous. These two factors restrict the commercial production of aerogels. So it is necessary to fabricate the silica aerogels using a low-cost precursor in combination with a cheap and safe drying method. Sodium silicate is perhaps the cheapest industrial silica source, its chemical stability is long, easy to handle and has no flammability hazard like silicon alkoxides. Moreover, for drying step the ambient pressure drying (APD) method was proposed instead of supercritical method [27–29]. Hence, in this work the copper–silica aerogel nanocatalyst was synthesized using the sodium silicate as silica source and by simple drying at ambient pressure through the solvent exchange and surface modification of the wet gels.

Various methods such as kneading and ion exchange [30–33], deposition–precipitation [32,34], co-precipitation [32], impregnation [33,35–37] and sol–gel process [10,36,38,39] have been used for introducing the copper to the silica matrix in conventional silica-supported copper catalyst. In this work, wet gels were formed through sol–gel process by cogelation of active metal precursor and silica precursor. This method provides controllable loading of metal, higher dispersion, stronger anchoring of metal particles in the support and more stable catalysts than other methods [25,36,40,41].

However, there are a few studies concerning the copper–silica composite aerogels. Hair et al. [42] prepared copper–silica aerogel, but used silicon alkoxide, as Si source and drying by supercritical method. The influence of preparation condition on the structure of copper-doped silica composite aerogel was investigated by Li GuiAn et al. [43]. However, in their work in addition to using alkoxide precursor the drying control chemical additive (DCCA) was used to preserve the wet gel structure and avoid the collapse of the gel during the ambient drying. DCCA is usually used to manipulate pore size and decrease the capillary drying stresses and to convert the wet gel into a monolithic xerogel; in order to achieve the aerogel the addition of DCCA is followed by supercritical drying [44–46]. On the other hand, literature shows that the most common and successful preparation method for APD derived silica aerogels is the hydrophobication of gels through silylation of their pore surface by silylating agents such as TMCS and HMDS [27–29,47,48]. Hence, in the present work,

after obtaining the wet gels by cogelation of active phase and support precursors, the mentioned method was used to dry the wet gels. The prepared copper–silica aerogels were characterized by AAS, BET, XRD, TPR, SEM, TEM and FTIR techniques and their catalytic performance was evaluated in the MSR process to hydrogen production.

## Experimental

### Catalyst preparation

Initially, the sodium silicate solution ( $\text{SiO}_2$  contents 8 wt%,  $\text{Na}_2\text{O}:\text{SiO}_2$  mole ratio 1: 3.3, Merck) was diluted with the deionized water by 1:4 volume ratio, then this diluted solution was mixed by an ion exchange resin (IR-120, Merck) to replace the  $\text{Na}^+$  ions present in the water-glass by the  $\text{H}^+$  ions. Collecting the ion exchanged solution results in silicic acid (SA). The desired amount of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (Merck) was dissolved in deionized water by ultrasound stirring. This copper nitrate aqueous solution was added to SA and mixed vigorously. In order to achieve gelation, the resulting mixture was transferred into the air tight PTF beakers and aged at  $60^\circ\text{C}$  for 12 h. The resulting gel was immersed in equivolume isopropyl alcohol for 18 h. Then the pore liquid was exchanged with hexane two times during a 48 h period. Hexane was removed from beaker and for surface modification the gel was immersed in an equivolume solution of 20% HMDZ (Merck) in hexane at  $60^\circ\text{C}$  for 24 h. After the completion of surface modification reaction the resulting liquid was removed from the beaker and the obtained wet gel was dried at  $60^\circ\text{C}$  for 4 h,  $90^\circ\text{C}$  for 2 h and  $120^\circ\text{C}$  for 2 h. For calcination, the as prepared catalysts were heated up ( $4^\circ\text{C}/\text{min}$ ) to the desired calcination temperature (300, 450 and  $700^\circ\text{C}$ ) and kept at the final temperature for 3 h in a muffle furnace.

### Catalyst characterization

Atomic absorption spectrometry (AAS, Analytic Jena novAA 300, Germany) was used for obtaining the Cu contents in the aerogel catalysts. The BET surface area and pore size distribution of the catalysts were measured using instrument by nitrogen adsorption–desorption method (Belsorp mini II, Japan and Quantachrome Instruments CHEMBET – 3000, USA). X-ray diffraction (XRD) patterns were obtained with a BrukerAxs D8, Germany, diffractometer using  $\text{Cu K}\alpha$  radiation. Fourier transform infrared (FT-IR) spectra of the samples were obtained with a Mattson 1000 FTIR spectrometer, Unicam, UK. Spectra were recorded in the range of  $4000\text{--}400\text{ cm}^{-1}$ . The samples were diluted with IR-grade KBr.

Microstructural studies of the copper–silica aerogel catalysts were performed by Field Emission Scanning Electron Microscopy (MIRA3 FE-SEM, Tescan, Czech) and Transmission Electron Microscopy (CM30, Philips). Temperature programmed reduction (TPR) experiments were carried out using BELCAT, Japan, apparatus equipped with a thermal conductivity detector (TCD). 0.23 g of catalyst was placed in the reactor, then heated and reduced in a flow of 7.25%  $\text{H}_2/\text{Ar}$  mixture with a flow rate of 50 ml/min. The samples were heated from room temperature to  $850^\circ\text{C}$  and the heating rate was kept at  $10^\circ\text{C}/\text{min}$ .

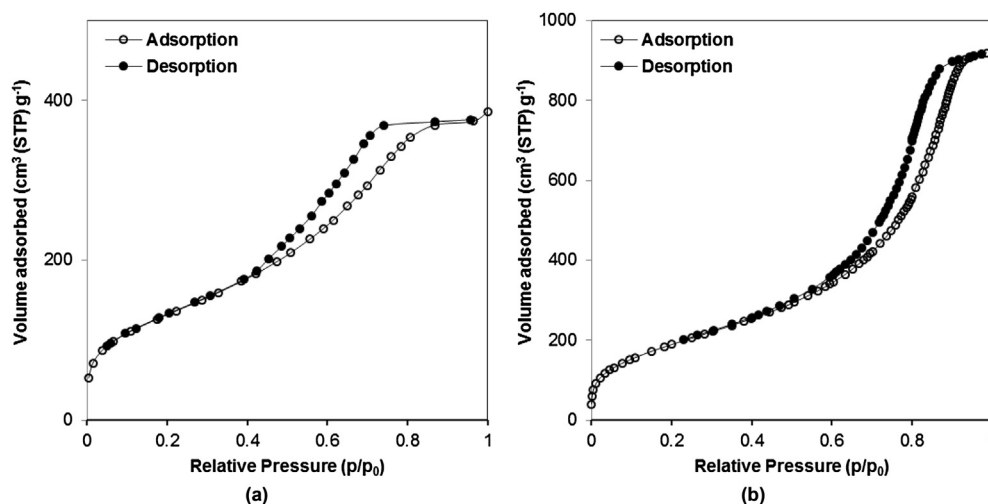


Fig. 1 – N<sub>2</sub> adsorption–desorption isotherms of the coaged copper–silica aerogel catalysts: a) 13.3Cu-700 and b) 7Cu-450.

### Catalyst testing

Catalytic activity and selectivity of the prepared copper–silica aerogels was tested in the methanol steam reforming for hydrogen production. The MSR reactions were performed in a tubular fixed-bed reactor with 4 mm ID over 300 °C at atmospheric pressure. 1.0 g of catalyst was loaded into reactor and pre-reduced by hydrogen flow at 300 °C for 2 h. The liquid flow with water/methanol molar ratio of 2/1 was fed using a liquid syringe pump (702 SM Titrino, Metrohm). Argon was used as carrier gas. The product gas which includes CO, CO<sub>2</sub> and H<sub>2</sub> was analyzed by Agilent Technologies7890 A GC with a capillary column (HP-Plot/Q, 30 m, 0.53 mm, 40 μm).

## Results and discussion

### Characterization

Due to the copper losses during the various steps of catalyst synthesis, the actual amount of copper in the final catalyst

was determined by AAS. Three samples were synthesized by adding various amounts of copper nitrate solution. The copper contents of the three samples measured by AAS are 4.1, 7.7 and 13.3% which showed 10–20% of the initial copper is lost during various steps of synthesis. The samples name is referred to as ACu-B in which A and B indicate the copper weight percent in catalyst and calcination temperature, respectively.

Fig. 1 shows the nitrogen adsorption–desorption isotherms of Cu–SiO<sub>2</sub> aerogel catalysts. The catalysts exhibited type IV isotherms which were given by mesoporous materials and a superposition of H1 and H2 hysteresis loops according to IUPAC classification, which suggests the presence of narrow distribution of cylindrical-like and ink-bottle shaped pores [21,49,50].

The pore size distributions of samples determined by BJH method are given in Fig. 2. The distribution was plotted as  $dv/dr$  versus  $r$  so that the integrated area under the plot would correspond to the pore volume. For the 13.3Cu-700 sample the pore size is between 1 and 10 nm with a relatively sharp peak around 2 nm suggesting uniform pore size, thus the contribution of pore size in the range of 1.5–5 nm in the pore volume of sample is 75% and the average pore size is 5 nm. The 7.7Cu-

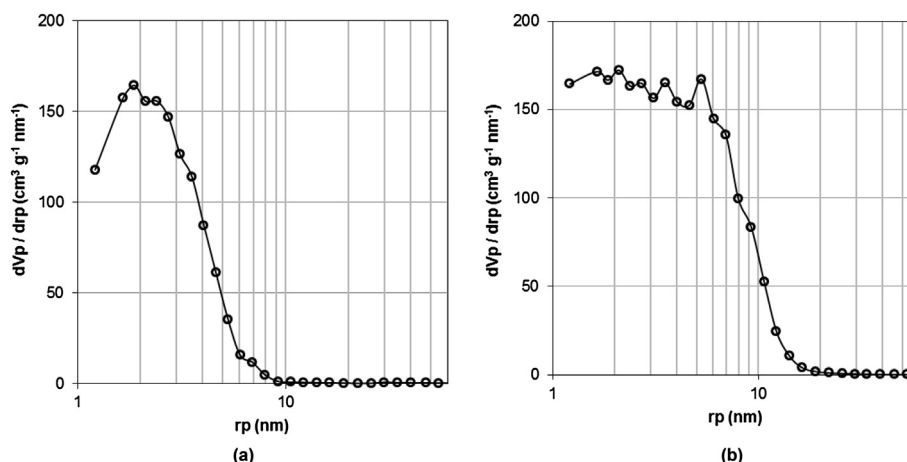
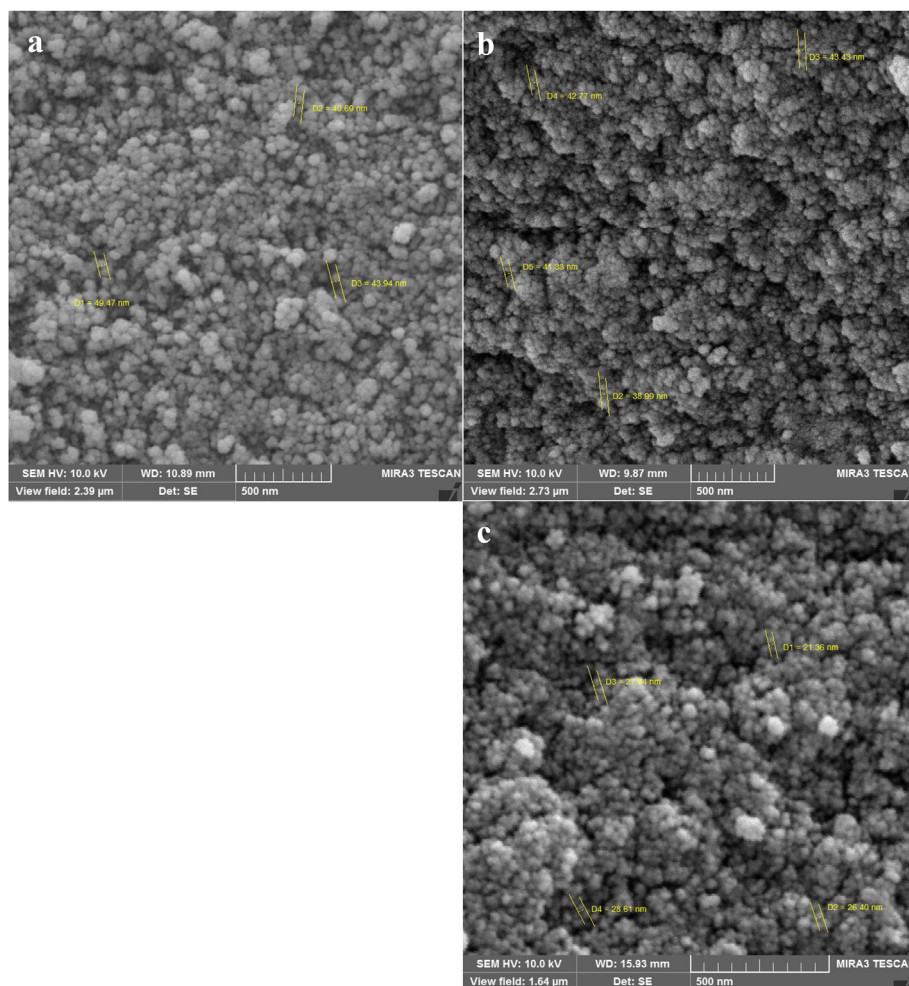


Fig. 2 – Pore size distribution profiles of the coaged copper–silica aerogel catalysts: (a) 13.3Cu-700 and (b) 7.7Cu-450.



**Fig. 3 – FE-SEM micrographs of the copper–silica aerogel catalysts: (a) 4.1Cu-450, (b) 7.7Cu-450 and (c) 13.3Cu-700.**

450 sample has a wider pore size distribution between 1 and 16 nm. The relatively horizontal plot between 1 and 8 nm shows the same contribution of these pore sizes in the pore volume. For this sample the average pore size is 8.3 nm and the diameter of 84% of pore volume is lower than 10 nm.

The surface morphology and pore structure of copper–silica aerogel catalysts observed from the FE-SEM pictures are shown in Fig. 3. It can be seen that the microstructure of catalysts was a three-dimensional nanoporous structure composed of fused spherical nanoparticles with good uniformity. The changes in the microstructure of copper–silica aerogel catalyst with various copper contents were not significant. However, as the copper content in the samples increased the copper–silica network became denser with small pore and particle size; so the specific surface area decreased, which was also confirmed by BET results which are shown in Table 1. Also, agglomeration of particles and the “cauliflower” shape of microstructure increased. In 4.1Cu-450

and 13.3Cu-700 samples the particle size was lower than 50 and 30 nm, respectively.

Further investigation of morphology and active metal distribution was done by TEM analysis and the result for 13.3Cu-700 sample is shown in Fig. 4. The TEM micrograph shows well-developed three-dimensional nonporous network in which highly distributed copper phase throughout the amorphous silica matrix was observed. As seen, it is difficult to clearly distinguish the copper oxide particles, this is due to the cogelation of copper and silica precursors in the sol–gel synthesis.

FTIR spectra of the as prepared and the calcined copper–silica aerogels with 13.3% wt of copper content are shown in Fig. 5. Three calcination temperatures of the samples were 300, 450 and 700 °C. The absorption peaks at around 1100, 800 and 470  $\text{cm}^{-1}$  are due to the asymmetric, symmetric and bending modes of the Si–O–Si bonds in the silica network [47]. In the as prepared aerogel the peak at 2970  $\text{cm}^{-1}$

**Table 1 – BET surface areas of prepared copper–silica aerogel catalysts.**

Sample Name	4.1Cu-450	7.7Cu-450	13.3Cu-300	13.3Cu-450	13.3Cu-700
Specific surface area ( $\text{m}^2/\text{g}$ )	836	719	621	514	476



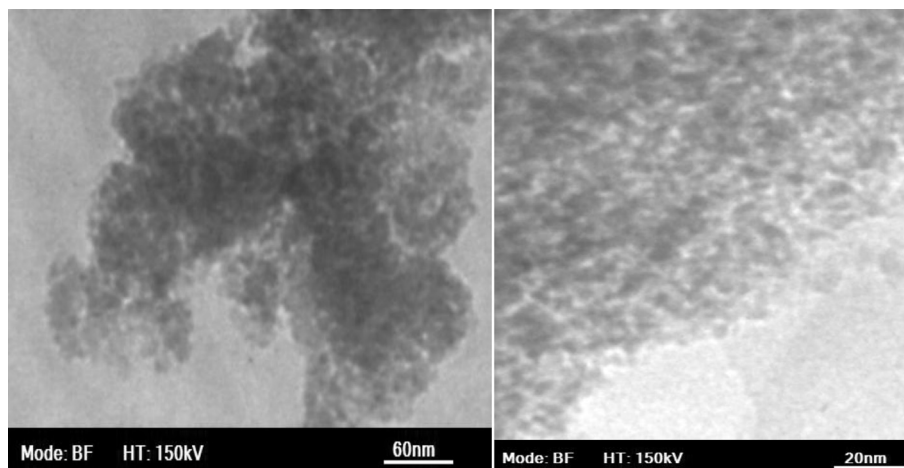


Fig. 4 – TEM images of the coaged copper–silica aerogel catalysts calcined at 700 °C.

corresponds to the C–H groups and the peaks around 850 and 1260  $\text{cm}^{-1}$  are related to the Si–C groups [47,51]. These groups resulted from the replacement of the surface H in the Si–OH by  $\text{Si}(\text{CH}_3)_3$  groups during chemical surface modification step. By calcination these bands gradually disappear because of breaking and decomposition of the carbon bonds such that the Si–C and C–H bands weakened in the 13.3Cu-300 and totally disappear in the 13.3Cu-450 and 13.3Cu-700 samples. Therefore, by calcination at 450 and 700 °C the initial hydrophobic copper–silica aerogel was converted to hydrophilic catalysts. The absorption peaks of CuO at 460, 500 and 575  $\text{cm}^{-1}$  [36,38] cannot be distinguished due to overlapping with the broad peak of Si–O–Si at 470  $\text{cm}^{-1}$ .

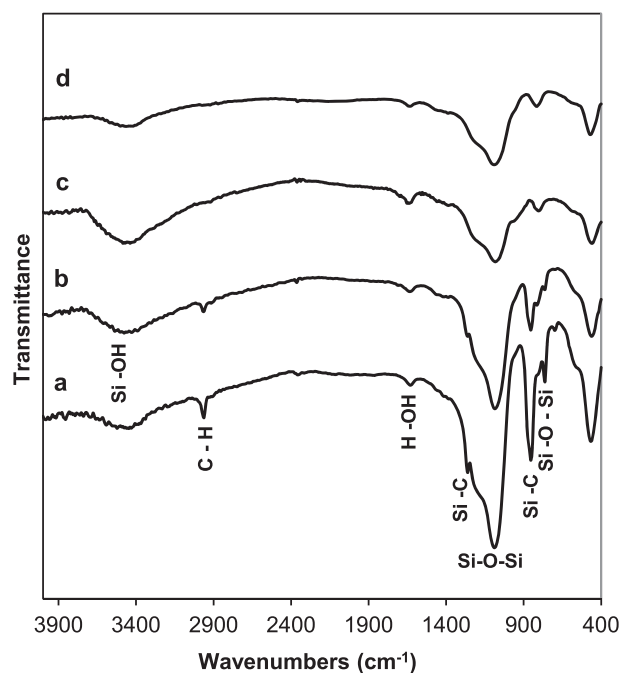


Fig. 5 – FTIR spectra of the coaged copper–silica aerogel catalysts with 13.3 wt% copper content: a) without calcination and calcined at (b) 300, (c) 450 and (d) 700 °C.

Fig. 6 shows the XRD patterns of the prepared samples. In the XRD patterns of four 4.1Cu-450, 7.7Cu-450, 13.3Cu-300 and 13.3Cu-450 samples no characteristic peak of any crystallite phase was observed, but there is a broad peak centered at 22° assigned to amorphous silica [36,52]. This indicates that copper species are amorphous or atomically dispersed and incorporate within the matrix during sol–gel synthesis, forming very small highly dispersed particles which are undetectable by XRD technique. For 7.7Cu-700, 13.3Cu-700 samples which calcined at 700 °C the characteristic peaks of copper oxide at 35.5° and 38.7° [10,36,52] and copper silicon at 34° appeared. At high temperature the decomposition of copper hydrosilicate and oxidation possibility of copper species which have strong interaction with matrix increases, and crystallization of CuO particles and copper–silicon compounds took place, so the corresponding peaks of the formed phases appear in the XRD patterns.

The TPR analysis was used in order to characterize the dispersion and state of metal species over and/or in the support and the interaction between metal species and support. The TPR-profiles of 7.7Cu-450 and 13.3Cu-700 samples are shown in Fig. 7. The TPR-profile of 7.7Cu-450 sample exhibits a peak around 210 °C which can be related to the presence of chrysocolla-like copper species in the aerogel catalyst. The olive green color of the sample confirms this result [32]. Indeed, as prepared copper–silica aerogel catalyst was blue, this is characteristic of hydrated copper ions in an octahedral environment [32,34]. Upon calcination, the copper hydrosilicate in the catalyst was dehydrated to form highly dispersed “chrysocolla” structure and the color of catalyst changed from blue to olive green, which is characteristic of chrysocolla compound. This result is in good agreement with the XRD result which showed no diffraction peak due to highly dispersed isolated copper ions. In the TPR-profile of 13.3Cu-700 sample a peak at higher temperature around 270 °C was observed. This peak can be ascribed to reduction of the crystalline CuO particles which was also seen in the corresponding XRD pattern. Whereas the copper–silica aerogel catalyst calcined at 450 °C was an olive green color, the samples calcined at 700 °C were black, characteristic of the formation of copper oxide in the catalyst precursor [33].

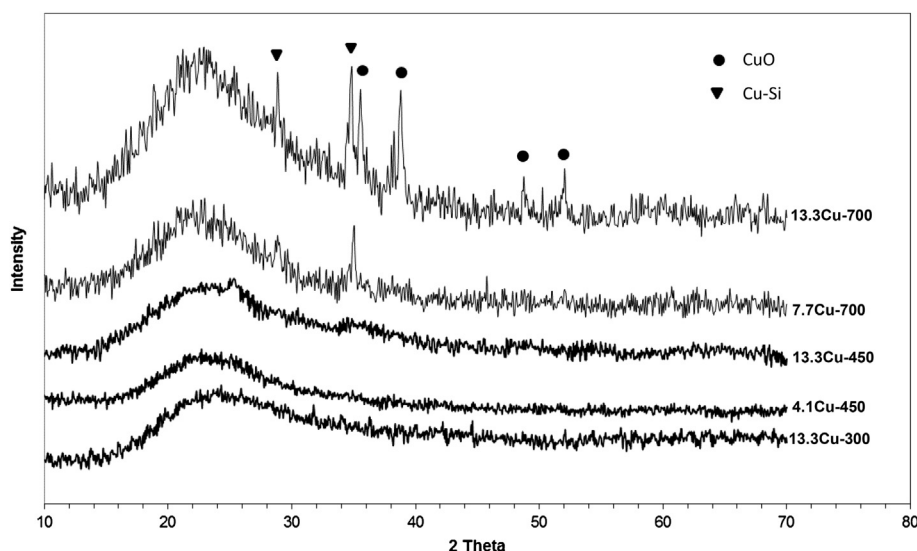


Fig. 6 – XRD patterns of prepared copper–silica aerogel catalysts.

Indeed, increasing the calcination temperature up to 700 °C results in the isolated  $\text{Cu}^{2+}$  copper ions in the samples calcined at 450 °C to cluster and transform into larger CuO and copper–silicon particles to disperse in the silica matrix. These larger and crystalline copper–silicon and CuO particles which were also detected by XRD analysis have strong interaction with matrix and reduced at higher temperature as seen from the TPR-profile.

#### Catalytic tests

The prepared copper–silica aerogel catalysts were used in the hydrogen production from methanol steam reforming process. The hydrogen production rate and CO selectivity obtained with commercial  $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$  catalyst and different

prepared aerogel catalysts are shown in Fig. 8. The copper content in the catalyst has a significant effect on the catalyst activity so that the hydrogen production rate for 13.3Cu-450 sample was approximately twice the  $\text{H}_2$  production rate of 7.7Cu-450 sample. Also, the higher calcination temperature improves the catalyst activity.

This observation indicates that the catalytic behavior of copper–silica aerogel depends on the chemical nature, dispersion of copper and particle size of copper during the reaction course. These properties depend on the copper loading and calcination temperatures. As illustrated by XRD and TPR results, the aerogels calcined at 450 °C include highly dispersed isolated copper ions enveloped within the  $\text{SiO}_2$  matrix which reduce to metallic copper with small particle size during the reaction course, while the CuO crystallite phase with higher reduction temperature is predominate on aerogel catalysts calcined at 700 °C. Thus, copper–silica aerogel catalyst with CuO primary species shows higher activity in the methanol steam reforming reaction. Similar results were obtained by Guerreiro et al. [52] and Wang et al. [36] who reported that the activity of CuO clusters is much higher in comparison with the highly dispersed Cu(II) ions in the methanol and 2-butanol dehydrogenation reactions.

Due to the poisoning effect of CO in the fuel cell and additional reactors requirements in order to remove CO from the fuel cell feed gas, the CO content in the reformer gas is an important criterion in the catalyst evaluation. In comparison with commercial catalyst with 39% wt of Cu, the 7.7Cu-450 and 13.3Cu-450 samples have lower activity but the 13.3Cu-700 sample showed higher activity. However, all prepared samples in the used operational conditions result in very low CO formation, so that no CO was detected (detection limit in the reactor effluent gas is 0.2%) by GC analyzer, whereas the CO selectivity with commercial catalyst was in the range of 6–11% for the used conditions.

This observation is in agreement with the reaction pathways reported in the literature. Two general mechanisms proposed for conventional  $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$  are the methanol

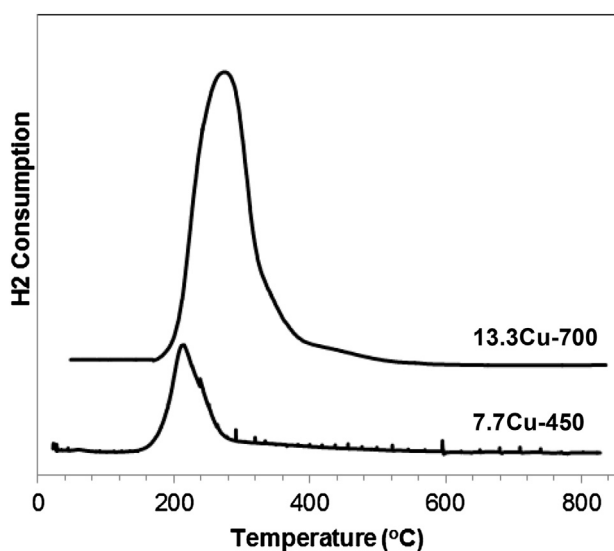


Fig. 7 – TPR profiles of the cogeled copper–silica aerogel catalysts.

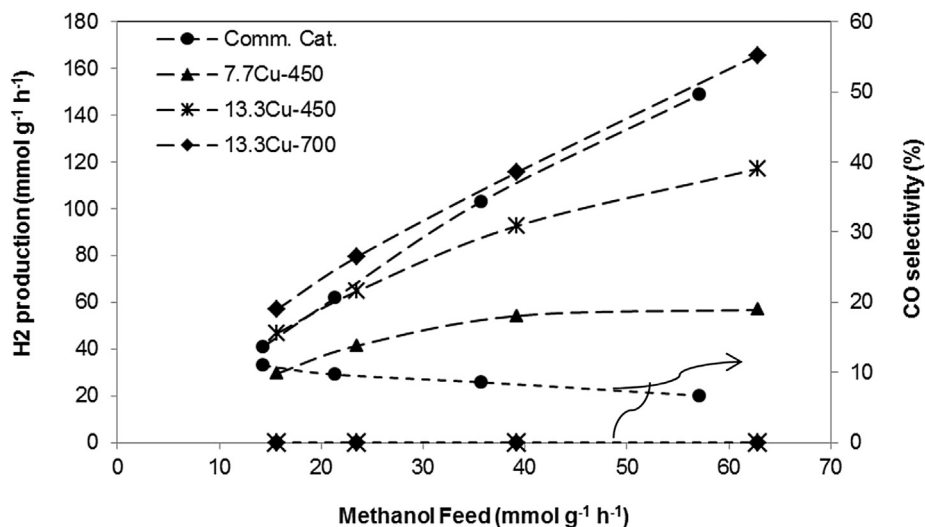
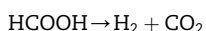
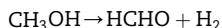
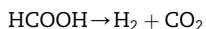
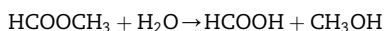
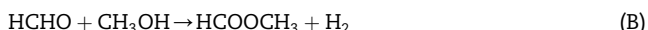
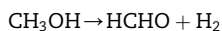


Fig. 8 – Catalytic activity and selectivity of the prepared cogeled Cu–SiO<sub>2</sub> aerogel catalysts and CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> commercial catalyst.

decomposition to CO and hydrogen followed by water–gas shift reaction, and the direct methanol reforming to CO<sub>2</sub> and hydrogen followed by reverse water–gas shift reaction [4,8,53,54]. While for Cu/SiO<sub>2</sub> catalyst, Takezawa et al. [55] and Takahashi et al. [56,57] proposed the mechanism of methanol steam reforming reaction as two pathways of A and B in which no CO participates.



and



However, CO can be produced through reverse water gas shift reaction depending on catalyst properties and operating condition which was not observed in our experiments conditions.

## Conclusions

Ambient pressure drying process was successfully applied to prepared copper–silica aerogel catalyst. The prepared aerogel catalysts exhibited attractive properties for catalytic applications such as high surface area, open porosity, nanostructure uniform morphology, highly and relatively uniform dispersed active phase within the silica matrix. Using the catalysts in the

methanol steam reforming reaction showed good hydrogen production rate and no CO detection in the optimum copper loading and calcination temperature. The catalytic tests promoted the proposed pathways for hydrogen production through MSR process and using Cu/SiO<sub>2</sub> catalyst in which no CO was produced.

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